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Chemical Interactions of Dissolved Silica With Iron (II) and (III)

John E. Schenk and Walter J. Weber Jr.

A paper presented on Jun. 8, 1967, at the Annual Conference, Atlantic City, N.J., by John E. Schenk, Research Fellow in Water Resources Eng., and Walter J. Weber Jr., Assoc. Prof. of Civ. and Water Resources Eng., both of the Dept. of Civ. Eng., Univ. of Michigan, Ann Arbor, Mich.

DISSOLVED silica is a major constituent of most natural waters; yet its significance in water quality transformations has remained largely undefined. One of the two most abundant elements in the earth's crust, silica is usually fourth or fifth highest in concentration of all dissolved species in natural fresh waters. It is thus important to develop systematic information regarding the effects of silica on the chemical and biologic characteristics of natural waters.

In defining the role of dissolved silica in water quality transformations, it is essential first to obtain sufficient information regarding the chemical nature of the various species of silica which may exist under different conditions in dilute aqueous solution. Secondly, considerations must be given to the chemical interaction of these species with other major components of natural waters, and with the various materials added in the course of water treatment.

This article describes some of the results of an investigation of several of the reactions of dissolved silica in dilute solution.

Solubility Relationships

Dissolved silica in natural fresh waters derives principally from the decomposition of aluminosilicate minerals, such as the feldspars.[1] Equations 1 and 2, the stoichiometric relationships for the formation of kaolinite and montmorillonite during the weathering of andesine (a plagioclase feldspar), clearly show examples of how silica may be released to natural waters.

$$\underset{\text{(Andesine)}}{Na_2CaAl_4Si_8O_{24}} + 4\,CO_2 + 14\,H_2O \rightarrow \underset{\text{(Kaolinite)}}{2\,H_4Al_2Si_2O_9} + Ca^{2+} + 2Na^+ + 4\,H_4SiO_4 + 4\,HCO_3^- \quad (1)$$

$$2\,Na_2CaAl_4Si_8O_{24} + 6\,CO_2 + 18\,H_2O \rightarrow \underset{\text{(Montmorillonite)}}{Na_2Al_6Si_{10}O_{30}(OH)_6} + 2\,Ca^{2+} + 2Na^+ + 6\,H_4SiO_4 + 6\,HCO_3^- \quad (2)$$

Field observations of the ratios of silica to bicarbonate and sodium (Si: HCO_3^- = 1:1; Si:Na^+ = 2:1 or 3:1) have been used by Feth *et al.*,[2] to verify that the weathering of silica-bearing minerals such as andesine is a major source of silica in many natural waters.

It is thus apparent that the maximum concentration of dissolved silica in a water must be a function of the solubility of the particular silica-bearing minerals with which the water

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comes into contact. For the case of crystalline quartz, the solubility limit would be approximately 10^{-4} moles Si/l (i.e., 6 mg/l as SiO_2) at normal temperatures and at pH values below 9.[3] The solubility of amorphous silica is considerably greater, however, and exhibits stronger temperature dependence. At 0°C the solubility of amorphous silica is about 1–1.3 millimoles/l (60–80 mg/l as SiO_2), while its solubility increases at 25°C to approximately 1.7–2.3 millimoles/l (100–140 mg/l as SiO_2).[4] In each case the solubility is enhanced by increasing pH values as a result of the formation of soluble silicate anions.[5] The appropriate equilibrium relationships are illustrated in reactions a through d in Table 1.

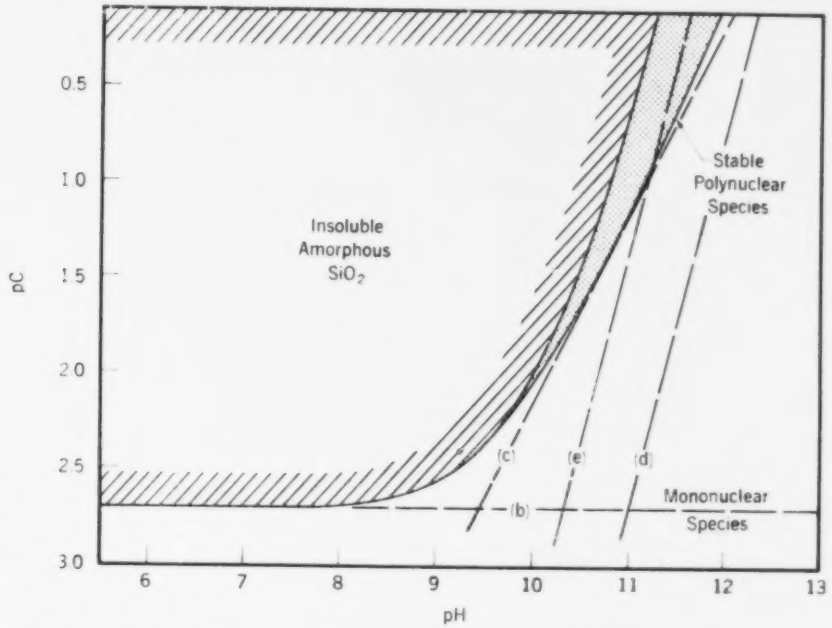

Fig. 1. Stability Diagram For Silica in Water

This diagram illustrates the variation in the maximum concentration expressed in terms of the negative logarithm, pC for various dissolved species of silica in equilibrium with amorphous silica as a function of pH at 25°C. Letters b–e refer to the corresponding equations given in Table 1. The shaded area defines the region of insolubility for amorphous silica; a solution of dissolved silica which is brought into this region either by increasing the silica concentration (decreasing the pC) or by decreasing the pH will undergo extensive polymerization and eventual gelation. The dotted area represents that pC-pH domain in which stable multinuclear species exist, and the remaining area, the conditions under which only monomeric forms are present.

It should be anticipated that the solubility limit for silica in waters equil-

ibrated with clays, feldspars, micas, and other siliceaous rock-forming minerals, will be between the values for crystalline quartz and amorphous silica.[7] That essentially all natural waters contain dissolved silica concentrations lying within this range of 6–120 mg/l has been demonstrated by Davis and DeWiest.[8] These investigators have published a series of frequency distribution curves for various major constituents of potable waters, which upon comparison illustrates additionally that silica exhibits the least variability in concentration of all species normally encountered in fresh waters. It must be recognized, however, that certain unique situations exist in water which can lead to silica concentrations much in excess of 120 mg/l. Because the solubility of amorphous silica is dependent upon temperature—up to 30–380 mg/l at temperatures in the range of 90°C—very high concentrations will very often occur in thermal springs. Similarly high concentrations may also be found in highly alkaline waters.

Although analytic data for silica are usually reported in terms of mg SiO_2 per liter, the silica exists essentially as monomeric ortho-silicic acid, H_4SiO_4, in most natural waters.[4] Because H_4SiO_4 is a very weak acid (refer to reactions c and d listed in Table I), the conjugate silicate anions are not present in significant concentrations in most natural waters in the pH range of 6–9. As Krauskopf[9] has noted, silica may exist in colloidal forms also, but in waters with total concentrations of silica less than 100 mg/l, any colloidal particles that are introduced are unstable and will disappear spontaneously within a short time.

Polymerization

A significant factor in any consideration of the aqueous chemistry of silica is the tendency of this material to undergo polymerization at sufficiently high concentrations to form polynuclear species. This aspect of the aqueous chemistry of silica is of concern in natural waters only in isolated instances

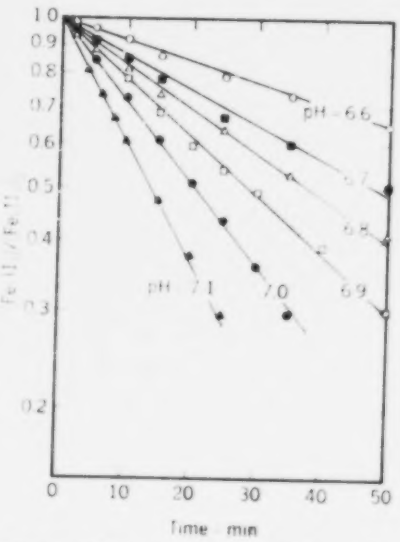

Fig. 2. Rates of Oxidation of Iron (II)

Observed rates of oxidation of ferrous iron at 25°C and a partial pressure of oxygen of 0.2095 atmospheres are illustrated for various values of pH in a bicarbonate buffer system. Linearization of the experimental data by plotting the ratio of observed to initial concentrations of ferrous iron on a logarithmic scale versus time indicates that the rate is first-order with respect to the concentration of ferrous iron.

where waters of high temperature or alkalinity with extremely high concentrations of silica mix with cooler, well buffered waters of lower pH. Polymerization phenomena are of considerable significance, however, for the use of activated silica for corrosion inhibition or as a coagulation aid.

It has been recognized for some time that dissolved silica, or silicic acid will, under supersaturated conditions, coordinate with hydroxo- or oxo-ligands to form multinuclear species, leading eventually to a gel network or colloidal solution. Despite several attempts to define the polymerization and gelation reactions that occur in acidified silicate solutions,[9-15] no completely satisfactory explanation of the chemical mechanisms involved in the formation of polysilicates or in the action of these polysilicates as coagulant aids or corrosion inhibitors has been advanced. Lagerstrom's[6] investigation of the first stages of polymerization has demonstrated reasonably well the presence of soluble species containing 2–4 silicon atoms, in addition to the stable monomeric acid and its conjugate base. A pH–pC stability diagram for silicic acid may be readily constructed from the equilibrium relationships established by Lagerstrom. This diagram, recently illustrated also by Stumm *et al.*,[16] is shown in Fig. 1.

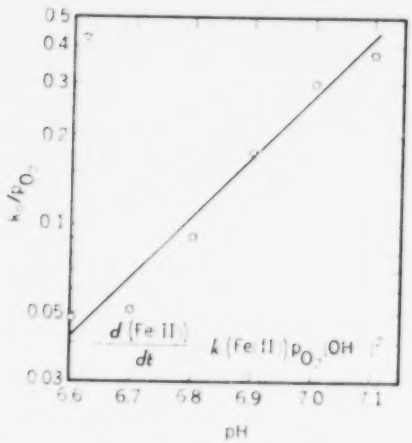

Fig. 3. Dependence of Oxidation Rate on pH

A logarithmic plot of values for the rate constant for oxidation of Fe (II) at 25 C divided by the partial pressure of oxygen on a logarithmic scale versus pH yields a linear trace with a slope of n = 2. The value of n = 2 indicates that the dependence of the rate of oxidation upon hydroxide concentration is of the second order. An increase in temperature will cause an increase in oxidation rate at a given pH; this can be accounted for in terms of the dependence of the ionization constant for water on temperature.

Qualitative evidence for the interaction of silicic acid with metal ions in aqueous solution was observed as early as 1933 by Mattson,[17] who suggested the existence of simple silicato-aluminum complexes to explain related observations made in the course of experiments on the electrodialysis of several different types of soils. This was followed in 1949 by the work of Hazel *et al.*,[18] in which interactions of silica with aluminum, iron, and chro-

Silica-Metal Ion Interactions

With pH–pC stability diagram for silicic acid may be readily constructed from the equilibrium relationships established by Lagerstrom. This diagram, recently illustrated also by Stumm *et al.*,[16] is shown in Fig. 1.

Although the stability curve shown in Fig. 1 indicates the respective pH-pC regions in which mononuclear and polynuclear species of dissolved silica will be prevalent, it is readily apparent that much more information regarding the exact nature and behavior of the polynuclear species is required. It is hoped that future work on the polymerization reactions of silica will more rigorously define the characteristics of the more important polynuclear forms. Such information is necessary for explanation of the mechanisms by which activated silica functions in coagulation and corrosion control.

mium were observed employing titrimetric procedures. Using more concentrated solutions, Yedava and Ghosh have studied the effects of dissolved silica on the conductivities of solutions of iron,[19] chromium,[20] barium,[21] and strontium.[21]

No quantitative relationships were established for any of these interactions until 1965, however, when Weber and Stumm [22] delineated the formation of a silicato-iron (III) complex, according to the following reaction:

$$Fe^{3+} + Si(OH)_4 + H_2O \rightarrow FeSiO(OH)^{2+} + H_3O^+ \quad (3)$$

These investigators covered an experimental pH range below 3.5 in their studies, in which only the free ferric ion and its first hydrolysis product are significant as far as iron (III) species are concerned. It is to be expected, however, that a similar relationship should exist between silica and iron (III) at pH values in the range corresponding to natural waters. Using the value of 1.8×10^9 obtained by Weber and Stumm as the stability constant for the silicato-iron (III) complex illustrated in Eq. 3, it can be shown that an acid mine water with a total silica concentration of 1 millimole/l (60 mg/l) and a total iron concentration of 0.1 millimole/l (5.6 mg/l) at pH 3 would have approximately one-third of the iron complexed with the silica. This extent of complexation can well be expected to exert considerable effect upon the chemical and biochemical characteristics of the water.

Oxidation of Iron (II)

A number of investigators have studied the kinetics of oxidation of iron (II) for several different types of aqueous systems. Study of iron oxidation in the buffer system of natural waters, however, has been limited to the early investigations of Just [23] and the more recent work of Stumm and Lee.[24] Stumm and Lee have shown qualitatively, the catalytic effects

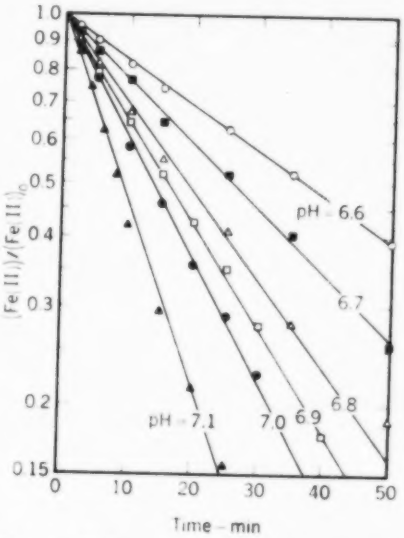

Fig. 4. Rates of Iron (II) Oxidation in the Presence of Silica

Observed rates of oxidation of ferrous iron at 25°C and $p_{O_2} = 0.2095$ atmospheres in the presence of 1 millimole/l of H_4SiO_4 in bicarbonate buffer solutions of different pH. Solid lines are the results of calculations utilizing Eq 8.

of various dissolved phosphate species on the rate of oxidation of iron (II). Huffman and Davidson [25] have stated that the rate of oxidation of iron (II) is dependent upon the anion present, and increases as the complexing affinity of the anion to ferric ion increases. These authors have hypothesized that the strength of anion complexes with

ferrous iron should follow the same order as with ferric iron. Ferrous-anion complexes may, therefore, be more significant in the oxidation reaction than the ferric-anion complexes.

As previously noted, silica has been shown by Weber and Stumm [22] to form a moderately strong complex with ferric iron. Thus, one might well anticipate that this material should show a pronounced effect on the rate of oxidation of iron (II), similar to the effect shown by phosphate because the stability constants are nearly the same for the iron (III) complexes of phosphate and silicate.[22, 26]

TABLE 1

Equilibrium Relationships Among Dissolved Species of Silica

Reactions	pK at 25 C	Reference
a. SiO_2 (Quartz) + $2H_2O$ = $Si(OH)_4$	3.7	3
b. SiO_2 (Amorph) + $2H_2O$ = $Si(OH)_4$	2.7	4
c. $Si(OH)_4 = SiO(OH)_3^- + H^+$	9.46	6
d. $SiO(OH)_3^- = SiO_2(OH)_2^{2-} + H^+$	12.56	6
e. $4Si(OH)_4 = Si_4O_6(OH)_6^{2-} + 2H^+ + 4H_2O$	12.57	6

The objectives of the present investigation have been to evaluate quantitatively, the catalytic effect of silica on the kinetics of iron (II) oxidation. The oxidation experiments, carried out in a manner similar to that used by Stumm and Lee,[24] were performed in bicarbonate buffer systems, thus simulating conditions in natural waters. All experiments were conducted with dissolved ferrous iron concentrations not exceeding 5×10^{-5} moles/l in order to prevent precipitation of ferrous carbonate. No precipitation or floc formation was observed during the course of any run.

Stock iron solutions were prepared by dissolving ferrous perchlorate in deoxygenated distilled water that was 0.1 *M* in perchloric acid. The proper volume of stock solution was then introduced into a bicarbonate buffer solution in a 2-liter glass reaction vessel to bring the total volume of the system to 1.5 liters. The reaction vessel was fitted with a lucite cover with ports for electrodes, stirrer shaft, gas line, thermometer, and sample withdrawal.

The solution in the reaction vessel was mixed continuously at 900–1,100 rpm by a motor-driven plastic-coated stirrer, and the entire vessel was immersed in a water bath to maintain the temperature of the solution at 25 (±0.5) °C. The alkalinity ranged from 30–50 me/l. A constant partial pressure of 0.2095 atmospheres of oxygen was maintained by bubbling analytic-grade dry air through the system continuously. Control of pH was accomplished by addition of carbon dioxide through a solenoid valve actuated by a signal from a potentiometric sensor in the reaction vessel. This allowed continuous maintenance of pH within 0.05 units.

The course of the reaction was followed by withdrawing 10-ml aliquots from the reaction vessel at suitable time intervals. These samples were quenched immediately in sulfuric acid to stop further reaction, and the concentration of ferrous iron in each was then determined by the bathophenanthroline method,[27] utilizing a double extraction with hexanol to insure quantitative separation.

Rates of Oxidation

The rate of oxidation of ferrous iron in a pure bicarbonate system has been shown to be a function of iron (II) concentration, partial pressure of oxygen, pH, and temperature.[24] The relationship expressing the dependence of oxidation rate on these parameters is given in Eq 4, in which k is the reaction rate constant, [Fe(II)] is the molar concentration of ferrous iron, p_{O_2} is the partial pressure of oxygen, and [OH$^-$] is the molar concentration of the hydroxide ion.

$$-\frac{d[\mathrm{Fe(II)}]}{dt} = k[\mathrm{Fe(II)}]p_{O_2}[\mathrm{OH}^-]^2 \quad (4)$$

It is apparent from Eq 4 that the reaction rate is of the first order with respect to iron (II) and oxygen but has a higher order of dependence on the hydroxide-ion concentration. Temperature is only involved as it affects the ionization constant, K_w, of water; the activation energy of the reaction is approximately zero when the hydroxide ion is considered the variable as in Eq 4. If the hydronium-ion concentration is taken as the variable, by substituting $K_w/[H_3O^+]$ for [OH$^-$] in Eq 4, there is a finite activation energy involved. The first-order dependence of the oxidation rate upon both ferrous-iron concentration and oxygen partial pressure has been established for several different systems,[24, 25, 28] and has been explained in terms of the Weiss radical mechanism.[29] As the concentration of ferrous iron enters the rate relationship to the first power, a plot of the logarithm of the iron concentration as a function of time should yield a linear trace. This same relationship should, of course, hold for the ratio of the iron (II) concentration at any time to the initial iron concentration, $[\mathrm{Fe(II)}]_o$, as may be observed in Fig. 2 for pure bicarbonate buffer systems.

The order, n, to which the hydroxyl ion enters the reaction given in Eq 4 may be obtained by plotting the logarithm of the rate of oxidation, $d[\mathrm{Fe(II)}]/dt$, divided by the partial pressure of oxygen, p_{O_2}, as a function of the logarithm of the hydroxide concentration, or simply against pH, as shown in Fig. 3. The slope of $n = 2$ which occurs in Fig. 3 for the present experimental data illustrates that the dependence of the rate of oxidation upon the hydroxide-ion concentration is of the second order; this concurs with the results of previous work.[23, 24] The value of 2.1 (±0.5) × 10^{13} liter^2 mole^{-2} atm^{-1} min^{-1} obtained for the overall rate constant, k, is also in general agreement with previous work.[23]

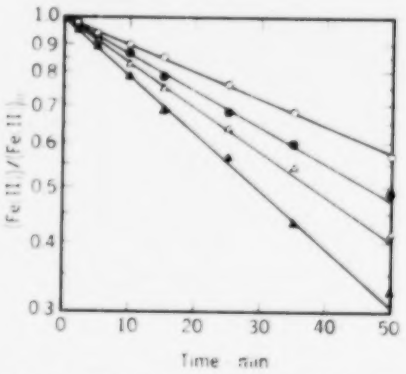

Fig. 5. Rates of Iron (II) Oxidation at pH 6.7 as a Function of Silica Concentration

Observed rates of oxidation at 25°C and $p_{O_2} = 0.2095$ atmospheres for pH 6.70. H_4SiO_4 concentrations are: ○ = zero, ● = 0.1 mmol/l, △ = 0.5 mmol/l, ▲ = 1 mmol/l. Solid lines were constructed by use of Eq 8.

Catalytic Effect of Silica

The catalytic effect of silica has been tested in these studies using much

the same experimental technique described previously for oxidation studies in pure bicarbonate buffer systems, except that sodium metasilicate was continuously mixed in the buffer solution at the appropriate pH and temperature for 30 min prior to addition of the stock ferrous iron solution. Once again aliquots were withdrawn for analysis of ferrous iron concentration at selected intervals, and the logarithm of the normalized iron concentration, $[Fe(II)]/[Fe(II)]_0$, was plotted as a function of time. As in Fig. 2 for the pure bicarbonate buffer systems, the data obtained for silica yielded a linear trace, indicating that the first-order dependence of rate upon ferrous-iron concentration was maintained in the systems containing silica.

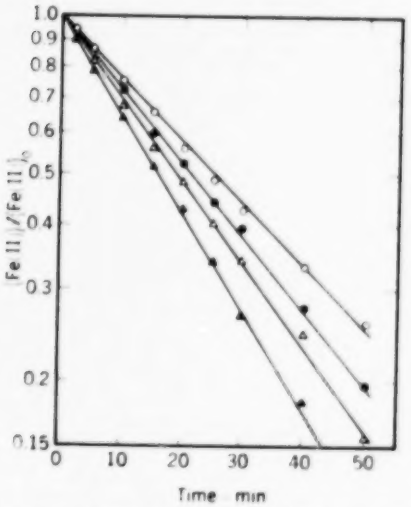

Fig. 6. Rates of Iron (II) Oxidation at pH 6.90 as a Function of Silica Concentration

Observed rates of oxidation at 25°C and $p_{O_2} = 0.2095$ atmospheres for pH 6.90. H_4SiO_4 concentrations are: ○ = zero, ● = 0.1 mmol/l, △ = 0.5 mmol/l, ▲ = 1 mmol/l. Solid lines were based upon calculations utilizing Eq 8.

It was observed throughout the pH range investigated (6.6–7.1) that rate of oxidation was increased by increasing the concentration of silica. Rates of oxidation obtained at two different pH values for a series of silica concentrations are shown in Fig. 5 and 6. In attempting to derive an empirical relationship to allow for prediction of oxidation rate in silica-bicarbonate systems, it was noted that the catalytic effect of silica is additionally a function of hydroxide-ion concentration. It is to be expected that the hydroxide-ion concentration (or pH) will dictate the species distribution of the monomeric silicic acid, and thus should have an effect on iron-silica complexation reactions.

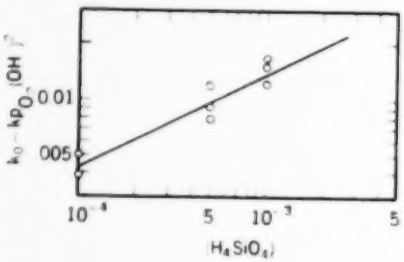

Fig. 7. Catalytic Effect of Silicic Acid on Iron (II) Oxidation

A plot of the logarithm of the apparent increase in oxidation rate versus the logarithm of H_4SiO_4 for various pH values results in a family of lines with a common slope of 0.5, indicating a 0.5 order dependence of oxidation rate on the silicic acid concentration. One such line, for pH = 6.9, is plotted in this figure to illustrate the observed dependence.

One of the most rational relationships for empirical description of the

catalytic effect of silica would be a rate expression of the form:

$$-\frac{d[Fe(II)]}{dt} = [k p_{O_2}[OH^-]^2 + k_{si}[H_4SiO_4]^n(1 + k'[OH^-])][Fe(II)] \quad (5)$$

The left side of Eq 5 is the observed rate of oxidation, k_o, and the first term on the right side is the rate obtained in a pure bicarbonate system. The term, k_{si}, the rate coefficient for the catalytic effect, n represents the power-dependence on silica concentration, and the term $(1 + k'[OH^-])$ indicates the dependence on hydroxide-ion concentration. The term $(1 + k'[OH^-])$ is descriptive in that it accounts for the functional dependence of the distribution of monomeric silica species ($H_4SiO_4 - H_3SiO_4^-$) on pH.

The dependence of the catalytic effect on the partial pressure of oxygen was not specifically studied. Although there is no experimental evidence to so indicate, it is possible that this effect may vary with p_{O_2}. In the absence of any such evidence, however, it has been deemed desirable to exclude p_{O_2}, which was held constant in the present experiments from the second term in Eq 5. It must be recognized, however, that there may be some possibility for the rate coefficient, k_{si}, to vary as a function of p_{O_2}.

Although Eq 5 provided a good description of the experimental data for experiments at pH 6.6 and 6.7, it proved increasingly inadequate as pH was increased. A second empirical relationship involving a power-dependence on $[OH^-]$ was therefore attempted. This relationship has the form:

$$-\frac{d[Fe(II)]}{dt} = (k p_{O_2}[OH^-]^2 + k_{si}[H_4SiO_4]^n[OH^-]^m)[Fe(II)] \quad (6)$$

in which m is indicative of the order of dependence of the catalytic effect upon $[OH^-]$, and all other terms are as previously defined. Eq 6 correlated the experimental data over the entire pH range studied, and has been used for description of the catalytic effect of silica on oxidation of iron (II).

To evaluate the constants in Eq 6, it is convenient to integrate this equation and express it in logarithmic form:

$$\ln(k_o - k p_{O_2}[OH^-]^2) = \ln k_{si} + n \ln[H_4SiO_4] + m \ln[OH^-] \quad (7)$$

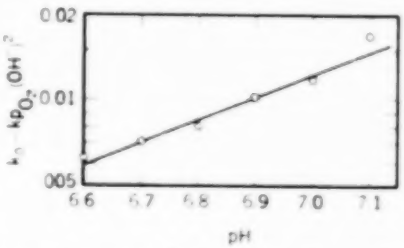

Fig. 8. Catalytic Effect of Silicic Acid as a Function of pH

A plot of the logarithm of the increase in oxidation rate versus pH results in a family of parallel lines for various H_4SiO_4 concentrations with a slope of 0.5. The line obtained for $[H_4SiO_4] = 5 \times 10^{-5}$ is plotted in this figure as an example to illustrate the observed relationship.

in which k_o is the observed rate of oxidation. Now, a plot of the logarithm of the effective increase in oxidation rate, $(k_o - k\ p_{O_2}\ [OH^-]^2)$, versus the logarithm of the silica concentration at a given pH should yield a linear trace. This is the case for the data from the present experiments, as illustrated in Fig. 7. In like manner, the logarithm of the increase in rate plotted as a function of the logarithm of the hydroxide-ion concentration (or versus

pH) for a given concentration of silica should yield a straight line, as shown in Fig. 8.

It may be observed in Fig. 7 and 8 that the slope of the line in each case is 0.5; thus, the final relationship obtained from the present experiments for the catalysis of iron (II) oxidation by dissolved silica in a bicarbonate buffer system, expressed in terms of the rate of oxidation is:

$$\frac{d[Fe(II)]}{dt} = k_{p_{O_2}}[OH^-]^2 p_{O_2} + k_{s_1}[H_4SiO_4][OH^-]^2 p_{O_2}[Fe(II)] \quad (8)$$

in which $k = 2.1 (\pm 0.5) \times 10^{13}$ liter^2 moles^{-2} atm^{-1} min^{-1} and, $k_{s_1} = 1.8 (\pm 0.3) \times 10^{9}$ liter mole^{-1}.

Because silica is only one of many possible catalytic species present in natural water, it is apparent that application of the above rate relationships must be accompanied by appropriate consideration of the potential effects of such other species.

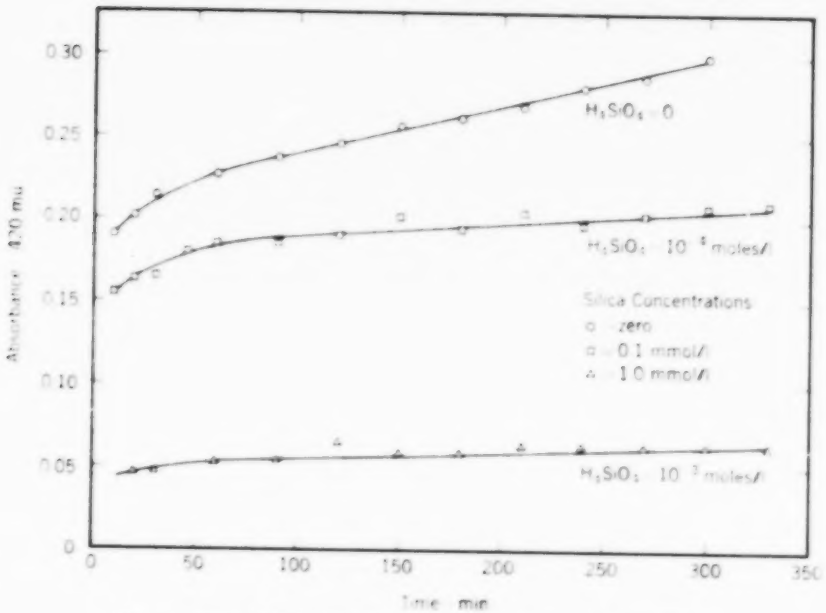

Fig. 9. Effect of Dissolved Silica on the Hydrolysis of Iron (III)

Absorbance measurements at 420 mμ performed on ferric iron solutions (0.1 millimoles/liter) at pH 2.5 and 25°C containing different concentrations of H_4SiO_4 indicate the retardant effect of the silica on the hydrolysis of the ferric iron.

Hydrolysis of Iron (III)

It is widely recognized that ferric iron undergoes extensive hydrolysis in aqueous solution under appropriate conditions of pH and concentration.[3] It is also quite evident that the hydrolytic reactions of iron (III) lead

to a very complicated system of hydrolysis products. This system is of considerable importance in water treatment technology because the hydrolysis products are important in the deferrization of iron-bearing waters by aeration and in the use of iron salts for coagulation. No previous study has been made of the effects of dissolved silica on the hydrolysis reactions of ferric iron. The previous work of Weber and Stumm [22] has established a quantitative reaction between iron (III) and dissolved monomeric silica, and because silica is present in most natural waters, it might be expected that the hydrolytic reactions of iron (III) would be affected in natural waters by silica.

In an attempt to obtain at least a qualitative indication of the effect of dissolved monomeric silica on the rate and extent of ferric iron hydrolysis, experiments have been conducted in which hydrolysis has been studied in bicarbonate systems in the absence and presence of various concentrations of dissolved silica and at different levels of pH. For all experiments, a stock solution of iron (III) was prepared by dissolving ferric perchlorate in 0.1 *M* perchloric acid to insure no premature hydrolysis.

Proper volumes of this stock solution were then added to rapidly stirred test solutions containing predetermined amounts of silicic acid and 10^{-2} moles/l of sodium bicarbonate, and the experiment started immediately. Prior to introduction of the iron stock solution at the initiation of each run, the silica-bicarbonate solutions were equilibrated for pH and temperature. All tests were run in the same reaction vessel described earlier for the oxidation rate studies; temperature was maintained at 25°C and the pH range was limited to values below 4 to retard the speed of the hydrolysis reaction sufficiently to permit study. Although this pH range is lower than would normally be encountered in natural waters, it is not much below that occurring in the solution to which ferric salts are added during slurry-feed or solution-feed coagulation operations. The silica concentrations used in the present experiments were below 2 millimoles per liter (120 mg/l as SiO_2) to insure that only monomeric species were present to any appreciable extent, and the iron concentrations ranged from 0.01–1 millimoles/l (0.56–56 mg/l). At appropriate time intervals, suitable aliquots were withdrawn from the reaction vessel for evaluation of the extent of hydrolysis.

Two different analytic techniques were employed. The first involved simple measurement of the absorbance of the sample at a wavelength of 420 mμ. This gave indication of the degree of color developed as a result of hydrolysis product formation. The second technique consisted of filtering the sample through a 0.45-μ membrane filter and determining the iron concentration in the filtrate by the standard phenanthroline method.[21]

Figure 9 is a plot of absorbance as a function of time for 10^{-4} *M* iron solutions containing different concentrations of silicic acid. It can be observed that color development due to hydrolysis is decreased markedly by the presence of dissolved silica. It would thus appear that the hydrolysis reaction is hindered by silica, possibly as a result of the competition of the silicic acid with water and hydroxide for coordination sites on the iron. The same general indication is given in Fig. 10, which shows that the percentage of

iron passing a 0.45-μ filter increases with increasing silica concentration. This again suggests the formation of a soluble complex between iron and silica which reduces the rate and extent of formation of hydrolysis products which would not pass the 0.45-μ filter. It is hoped that further work now being conducted in the authors' laboratory will further clarify these effects.

Conclusion

It is apparent from the present studies that dissolved monomeric silica, which is present in natural waters in concentrations ranging up to 120 mg/l, has marked effects upon rates of oxidation of ferrous iron and on the hydrolysis of ferric iron. Silica acts to catalyze the oxidation reaction, while it retards the hydrolysis of iron (III).

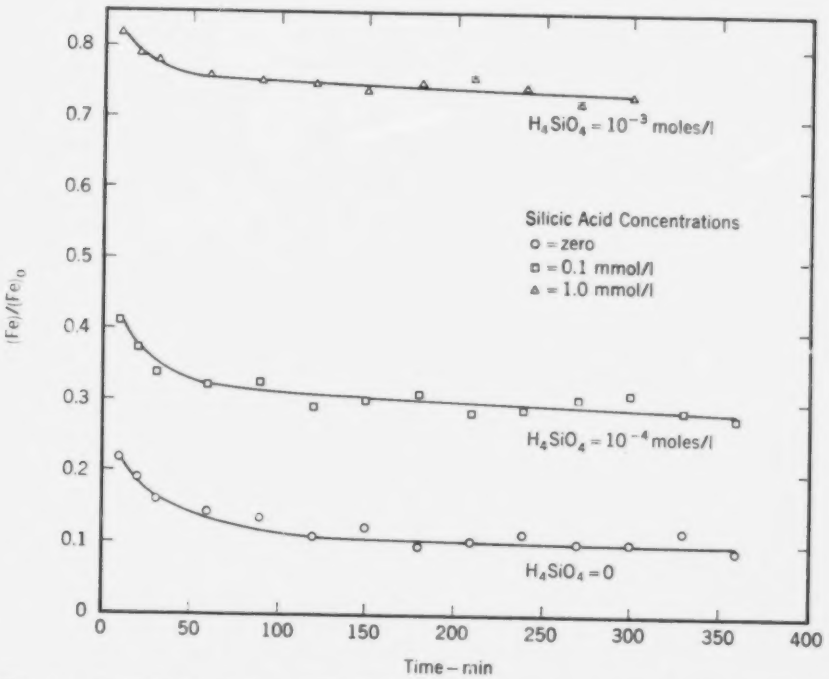

Fig. 10. Retardation of Iron (III) Hydrolysis by Dissolved Silica as Evidenced by Filtration Data

Samples of 0.1 millimolar Fe (III) solutions containing different concentrations of H_4SiO_4 at pH 3.5 and 25°C were filtered through a 0.45-μ filter at selected intervals. The ordinate on this plot is the ratio of Fe (III) concentration in the filtrate to that present initially in the test solution. It is apparent that more Fe (III) passes the 0.45-μ filter with increasing concentrations of H_4SiO_4, indicating once again the effect of the silica on reducing the formation of Fe (III) hydrolysis products.

The observed interactions of dissolved silica with iron (II) and (III) suggest several possible consequences for natural waters. First, complexes formed between silica and iron may alter the solubility relationships of dissolved iron in a given water, thus allowing a greater total iron concentration than would otherwise be possible. This alone may have considerable effects on the natural environment, both chemically and biologically. Second, the enhanced rate of oxidation of iron (II) in the presence of silica may allow more rapid and complete deferrization of iron-bearing waters, and may aid in explaining differences often noted between field observations and laboratory studies. Finally, in recognition of the role of chemical interactions in coagulation processes, the effects of silicic acid on iron hydrolysis may eventually help to explain the mechanisms by which polymeric-activated silica functions as a coagulant aid.

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